Multi-Functional Cathode Additives for Lithium-Sulfur Battery Technology

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Brookhaven National Laboratory

2017 Annual Merit Review

June 8, 2017

BROOKHAVEN NATIONAL LABORATORY

a passion for discovery

Stony Brook University

Project ID # ES281

Overview

Timeline

- Project start Oct. 2014
- Project end Sept. 2017
- 80% complete

Barriers

- Performance: Low Wh/kg (or L) & W/kg (or L)
- Cycle life: Poor cycle life
- Cost: High $/kWh

Budget

- Total project funding
  - FY 2015 $500K
  - FY 2016 $500K
  - FY 2017 $500K

Partners

- Brookhaven National Laboratory (BNL) (lead)
- Stony Brook University
- Columbia University

Relevance and Project Objectives

- **Overall Objectives**
  - Develop a low cost Li-S battery technology with high energy density for PEV application by incorporating multifunctional cathode additives (MFCA).
- **Project Relevance**
  - Our project efforts are directly aimed at addressing the barriers of Li-S battery low rate capability, polysulfide dissolution induced shuttling effect and limited cycle life.
- **Project Objectives This Period**
  - S-TiS_2 hybrid cathode formulation and process optimization.
  - Achieve high sulfur loading (> 6 mg cm^{-2}) with new binder and new carbon.
  - Optimize the S-TiS_2 hybrid electrode formulation and cell design factors for high power and long cycle life.
  - Mechanistic understanding of Sulfur-Metal Sulfide additive interaction via advanced characterization, including *in-situ/operando* characterization.

Approach/Strategy

- **Li-S Battery Technical Challenges**
  - Low sulfur utilization due to low conductivity of sulfur and Li_2S.
  - Polysulfide dissolution in electrolyte leads to low energy efficiency and fast capacity fade during cell cycling.
  - Slow reaction kinetics at 2.1V plateau discharge for high sulfur loading electrode.
- **Multi-Functional Cathode Additive (MFCA) Approach**
  - Electronically conductive
    - Promote sulfur cathode conductivity for high sulfur utilization.
  - Electrochemically active
    - Contribute to cell cycling capacity and compensate the extra weight.
  - Adsorbing polysulfide
    - Reduce polysulfide solubility for long cycle life.
  - Ionically conductive (Li^+ conductor)
    - Promote nucleation conversion of soluble polysulfide to insoluble Li_2S_2/Li_2S for high sulfur utilization and long cycle life, especially for high sulfur loading electrode.
- **Low Cost Approach**
  - Using low cost materials without complicated material processing.
  - Drop-in replacement electrode slurry casting manufacturing processes are used in this development.

Approach/Strategy

Phase I – Material Characterization and Optimization

Phase II – System Optimization

FY 2015				FY 2016				FY 2017			
Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4

Q3 2015 – Successfully demonstrated sulfur-MFCA interaction

Go/No-Go

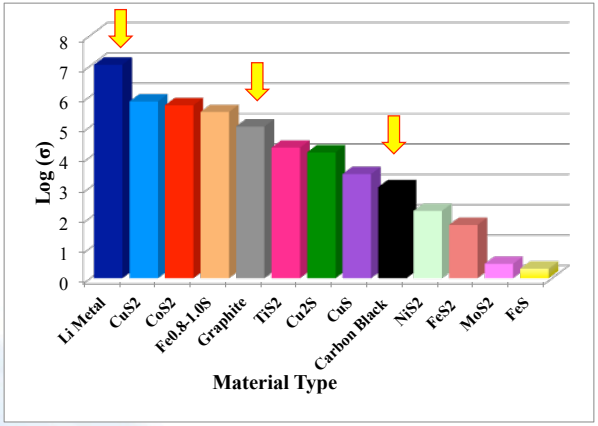
Q2 2016 – Improved cell cycling performance achieved for S:TiS_2 hybrid cathode

Go/No-Go

Focus on S:TiS_2 optimization

Q3 2017 – Finalize cell design and confirm cell performance output

Go/No-Go

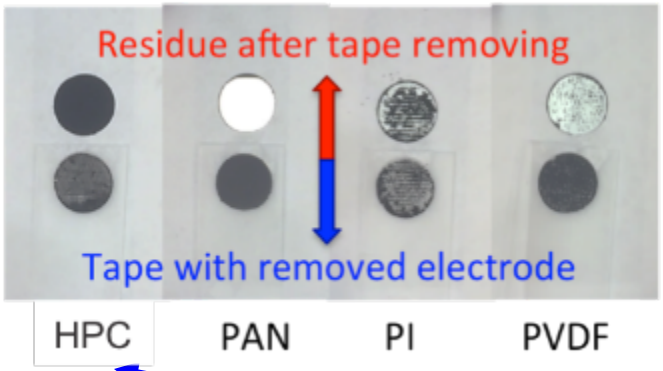


Metal Sulfide Electronic Conductivity

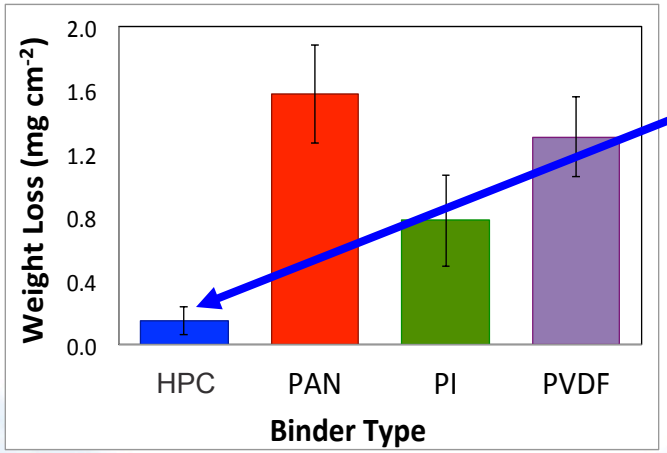
Date	FY / Quarter	Milestones/Achievement	Status
June, 2016	FY16 / Q3	Binder selection: Achieved good electrode mechanical integrity with no delamination	Completed
September, 2016	FY16 / Q4	Conductive carbon additive optimization: up to 10 mg/cm^2 sulfur loading achieved	Completed
December, 2016	FY17 / Q1	Cathode formulation optimization: Achieved >500 mAh/g (electrode)	Completed
March, 2017	FY17 / Q2	Cathode loading/density and power optimization	Completed
June, 2017 Go/No-Go	FY17 / Q3	Cell design and cell activation procedure development	On Schedule
September, 2017	FY17 / Q4	4 mAh cell sample preparation and confirmation study	On Schedule
All Year	All Year	Sulfur-Metal Sulfide additive interaction mechnanism understanding	On-going

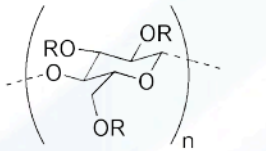
Accomplishments and Progress

Binder selection and cathode mechanical integrity



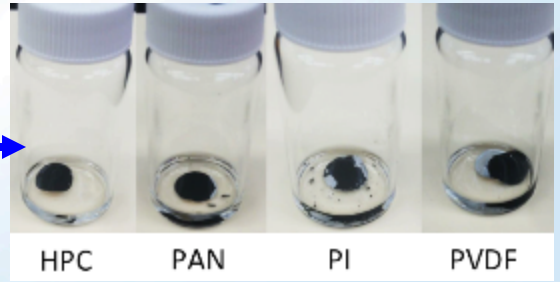
- Cathode delamination is detrimental to cell power and cycling performance
- Five binders have been evaluated for sulfur electrode
  - Hydroxypropyl Cellulose (HPC)
  - Polyacrylonitrile (PAN)
  - Polyimide (PI)
  - Polyvinylidene fluoride (PVDF) - control
  - Polyvinylpyrrolidone (PVP) – slurry not acceptable
- Achieved significant improvement on sulfur electrode mechanical stability/integrity with new HPC binder*
  - Superior adhesion to Al current collector
  - Good cohesion with low material-lost in tape test
  - Good adhesion to Al current collector after cell cycling test (100 cycles – similar coin cell performance)





HPC

R = H or $CH_2CH(OH)CH_3$

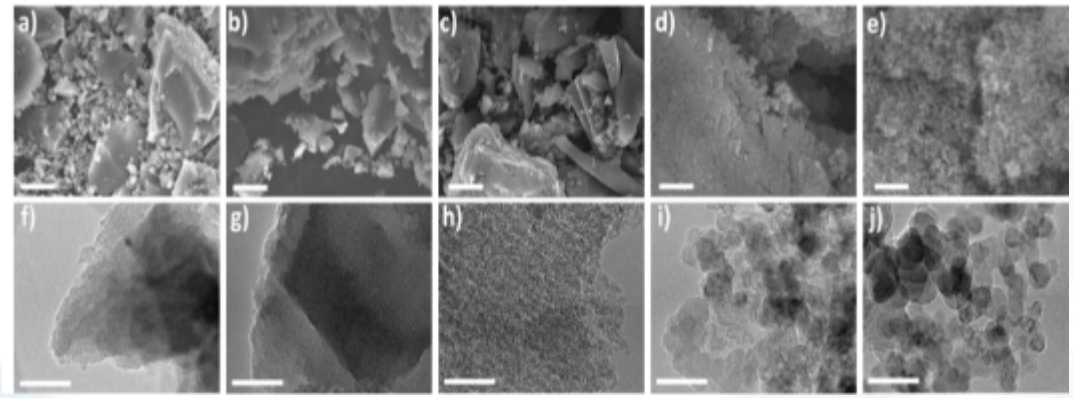


* Ke Sun, Christina A. Cama, Jian Huang, Qing Zhang, Sooyeon Hwang, Dong Su, Amy C. Marschilok, Kenneth J. Takeuchi, Esther S. Takeuchi, Hong Gan *Electrochimica Acta,* 235 (2017) 399-408, http://dx.doi.org/10.1016/j.electacta.2017.03.023

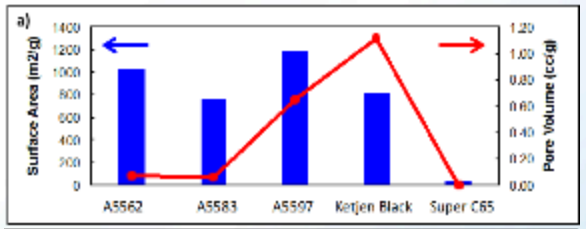
Accomplishments and Progress

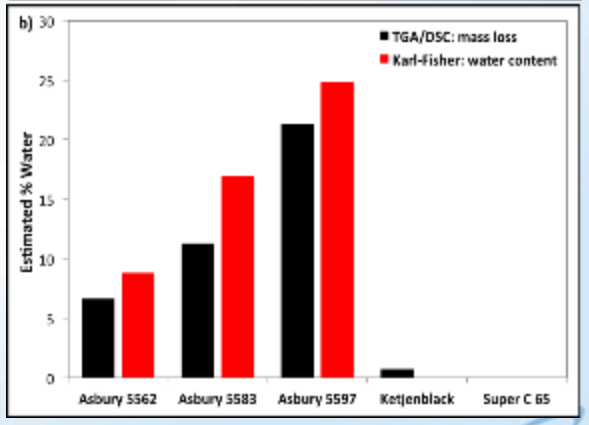
Carbon selection for high sulfur loading (> 6 mg/cm^2)

- Numerical cost analysis (*J. Electrochem. Soc.* 162 (2015) A982-A990) requires capacity loading of sulfur electrode to be higher than 8 mAh cm^{-2} in order to be competitive for the market (> 6 mg cm^{-2} sulfur loading is desired). Sulfur loading has profound effect on Li-S cell performance.*
- Our previous MFCA study utilizing Super C65 as conductive carbon in sulfur electrode, which can not achieve sulfur loading of > 3.6 mg cm^{-2} with either PVDF binder or HPC binder.
  - Severe cracks were observed for high sulfur loading samples after drying.
- Several commercial available micro-porous carbon materials with various particle sizes, surface areas and pore volumes have been evaluated for their impact on achieving high sulfur loading.**
  - Super C65 (control)
  - Ketjen Black
  - Micro porous carbon (A5562, A5583, A5597)



a)-e) SEM micrographs of A5562, A5583, A5597, Ketjen Black and Super C65, respectively, scale bar = 10 μm; f)-j) TEM micrographs of A5562, A5583, A5597, Ketjen Black and Super C65, respectively, scale bar = 100 nm.





*Ke Sun, Hellen Liu, Hong Gan, *J. Electrochem. En. Conv. Stor.* 13(2), 021002, **2016**.

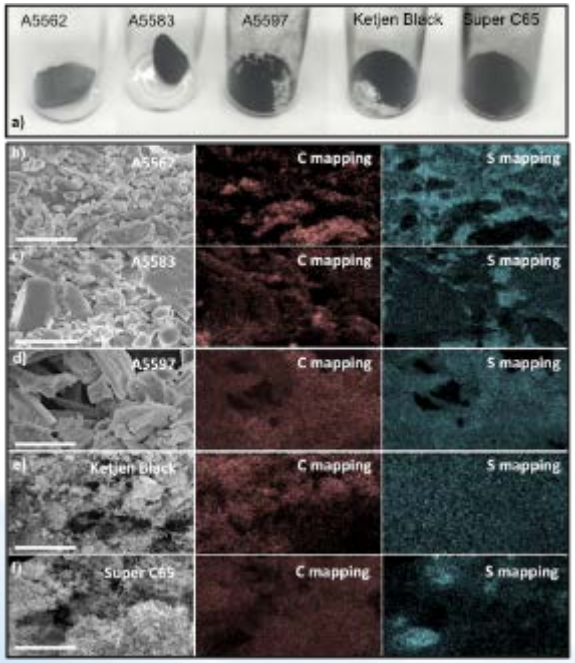
**Ke Sun, Christina A. Cama, Jian Huang, Qing Zhang, Sooyeon Hwang, Dong Su, Amy C. Marschilok, Kenneth J. Takeuchi, Esther S. Takeuchi, Hong Gan, *Electrochimica Acta,* 235 (2017) 399-408, http://dx.doi.org/10.1016/j.electacta.2017.03.023

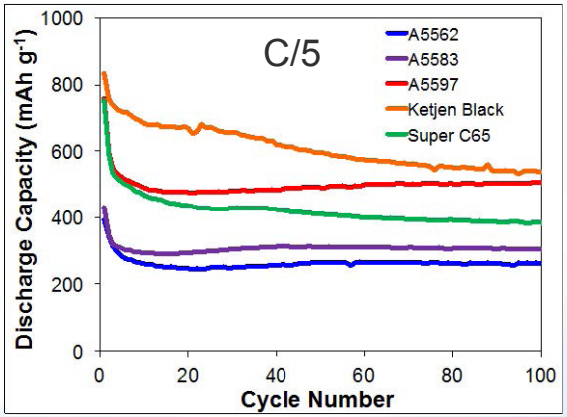
Accomplishments and Progress

Carbon selection for high sulfur loading (> 6 mg/cm^2)

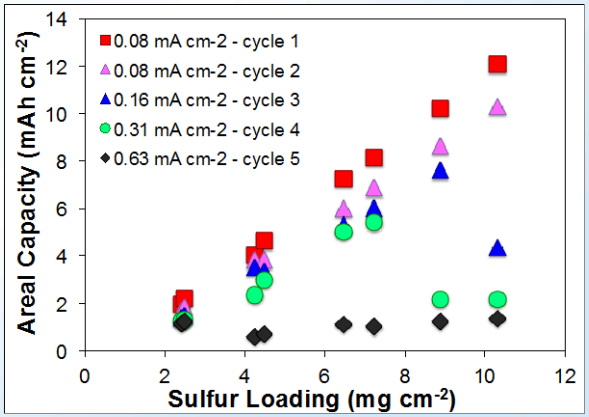
- Carbon with high pore volume (Ketjen Black and A5597) exhibits uniform sulfur distribution within the S-carbon composite after thermal fusion process.
- Carbon particle size strongly influences the ability in achieving high sulfur loading electrode.
  - Super C65 and Ketjen Black show electrode crack at sulfur loading higher than 4 mg cm^{-2}.
  - The other microporous carbons exhibit good electrode mechanical integrity with sulfur loading up to 10 mg cm^{-2}.

S-C composite after thermal fusion process





- A5597 identified as the leading carbon additive for high sulfur loading and stable cycle life.
- Achieved 10 mg cm^{-2} sulfur loading with up to 12 mAh cm^{-2} areal capacity delivery.*



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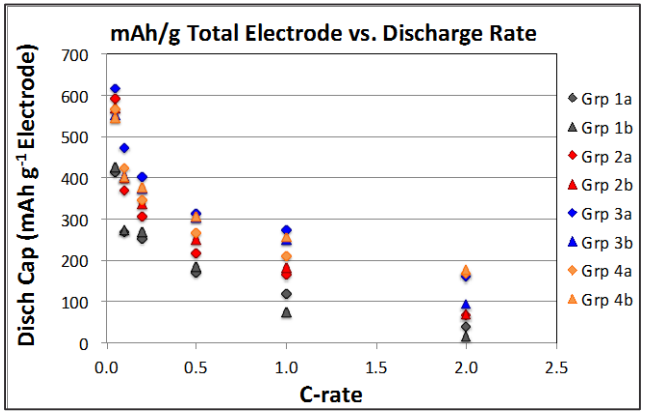
Accomplishments and Progress

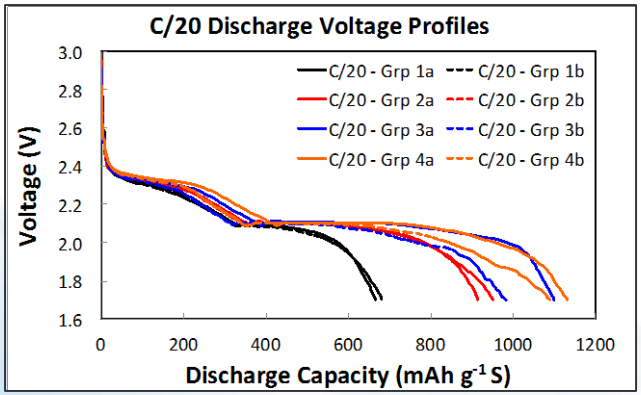
S-TiS_2 hybrid electrode formulation optimization

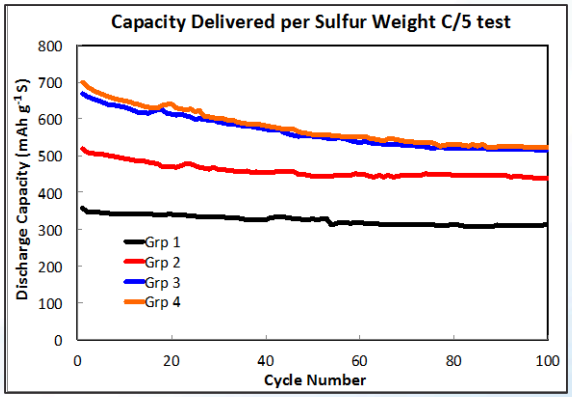
- As MFCA to improve sulfur utilization and cycle life, TiS_2 also contributes to the cathode weight.
- S-TiS_2 hybrid electrode formulation optimization for *energy density at electrode level*.

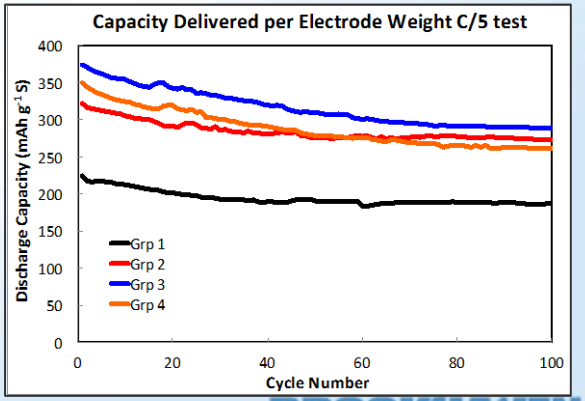
Group	Cathode Formulation (wt%)			
	Sulfur	Carbon	TiS_2	Binder
1	62.0	30.0	0.0	8.0
2	62.0	25.4	4.6	8.0
3	56.0	27.0	9.0	8.0
4	50.0	24.2	17.8	8.0



- The presence of TiS_2 enhances the sulfur utilization
- Delivered energy density at electrode level is not proportional to sulfur content – Group 3 formulation results in optimum electrode energy density.
- 600 mAh g^{-1} at the electrode level is achieved at C/20.



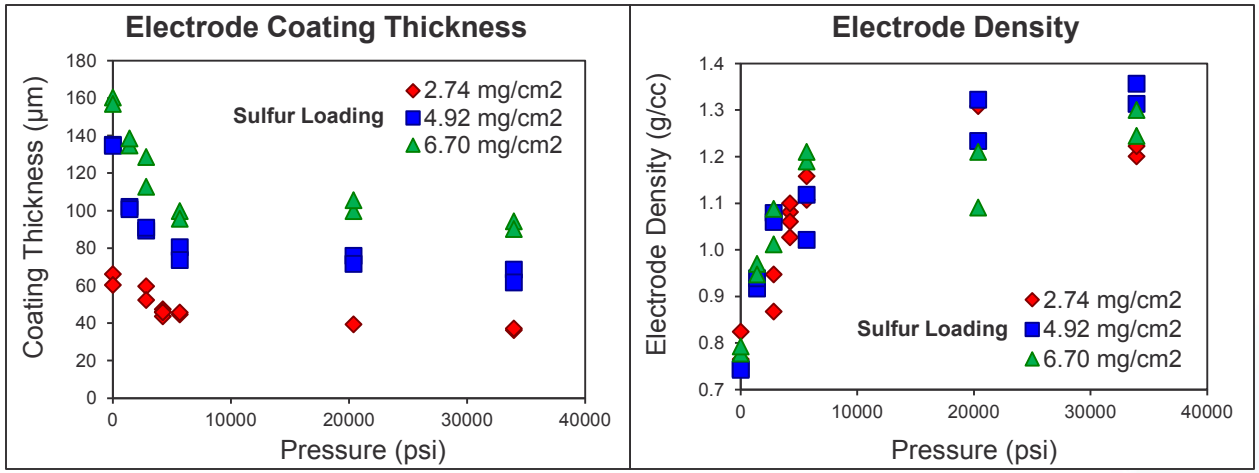




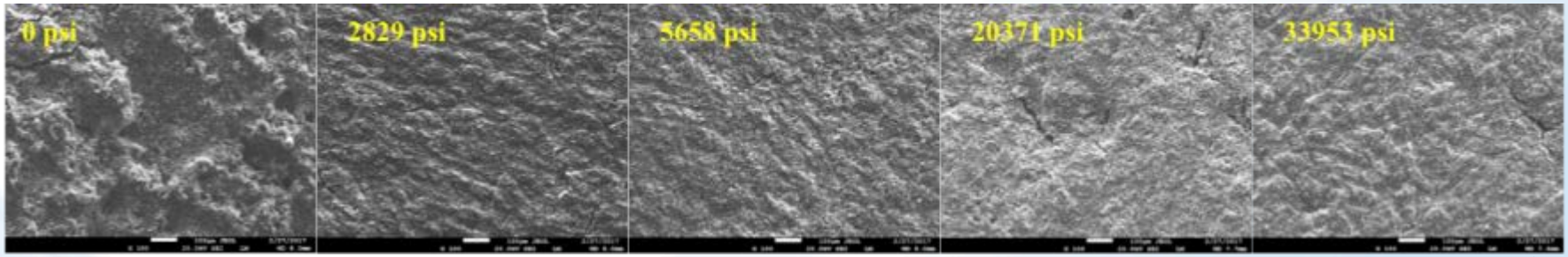
Accomplishments and Progress

Cathode density/loading vs. electrochemical performance

- Cathode density correlates to the cell energy densities (Wh/L and Wh/kg). It determines the volume (and weight) of electrolyte needed to fill the pores for ionic conductivity.



- Electrode density increases with the increase of the pressure.
- Electrode thickness and density leveling off at ~5000 to 10000 psi.
- Electrode surface becomes smooth after pressing.

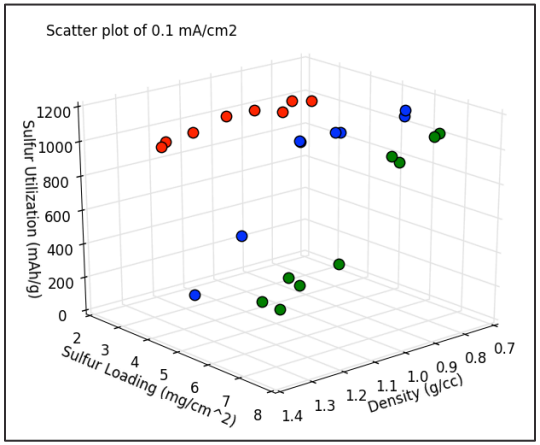


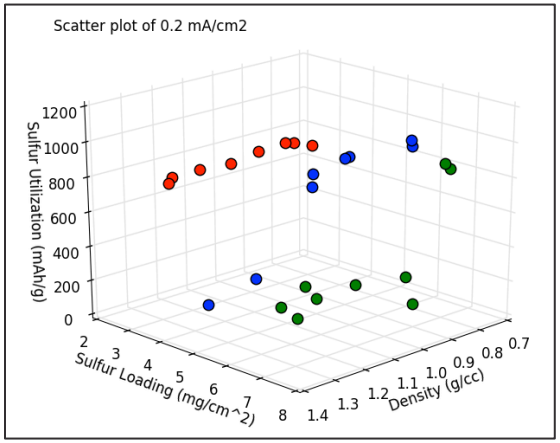
Electrode (4.92 mg cm^{-2} sulfur loading) Surface Morphology with Increased Pressing Pressure

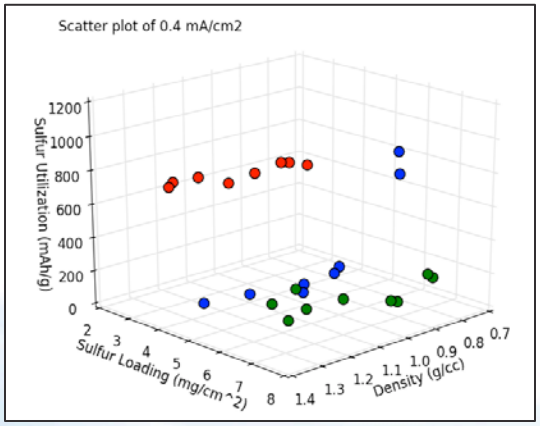
Accomplishments and Progress

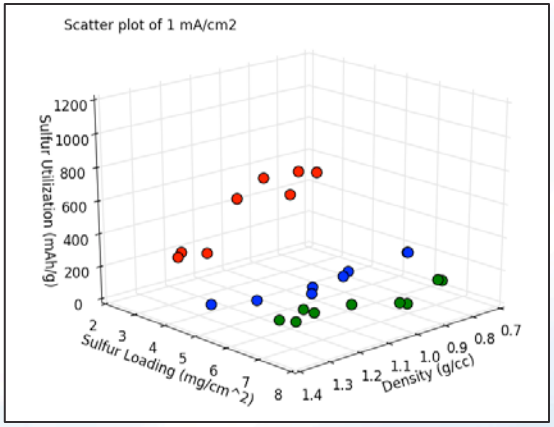
Cathode density/loading vs. electrochemical performance

- **Sulfur utilization vs. sulfur loading, cathode density and discharge current density**









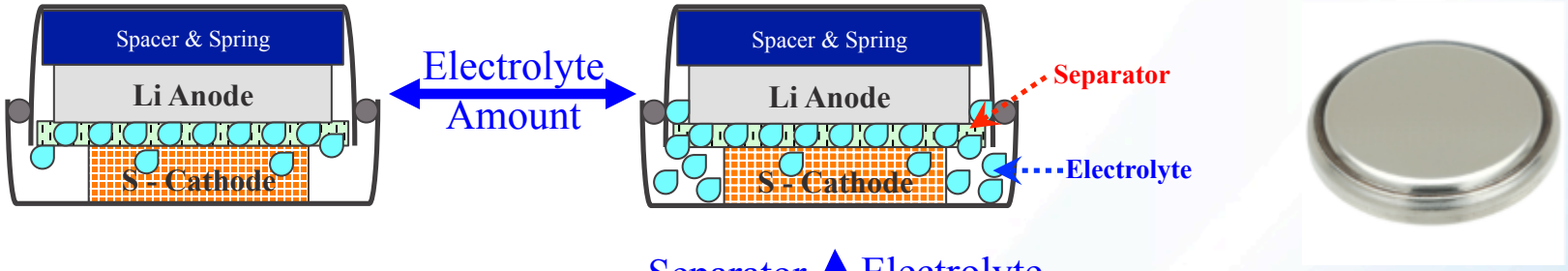
- The electrode density has profound effect on coin cell discharge performance and the impact is more significant on the higher sulfur loading electrodes and at higher discharge rates.
- Low sulfur loading and low electrode density favor the high sulfur utilization, especially at high current density discharge.
- Ionic conductivity and electrolyte conditions might be the primary root cause for the observed trend.

Accomplishments and Progress

Cell design optimization – electrolyte amount and location

- The impacts of electrolyte amount and electrolyte location in coin cells are evaluated

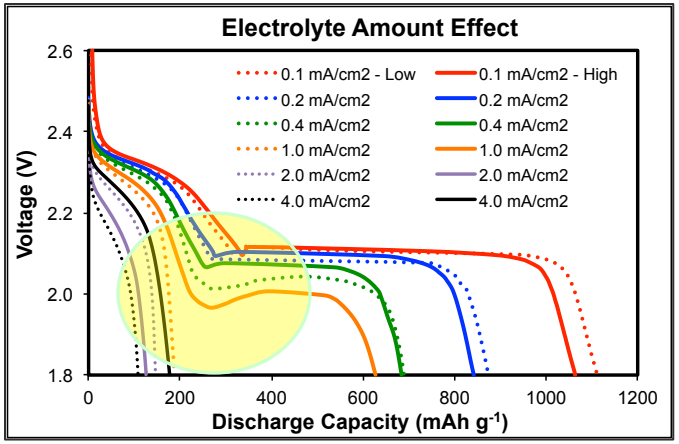
Group	Electrolyte Amount	Separator	Electrode Size
1	Low	Thin	Small
2	High	Thin	Small
3	High	Thick	Small
4	High	Thick	Large

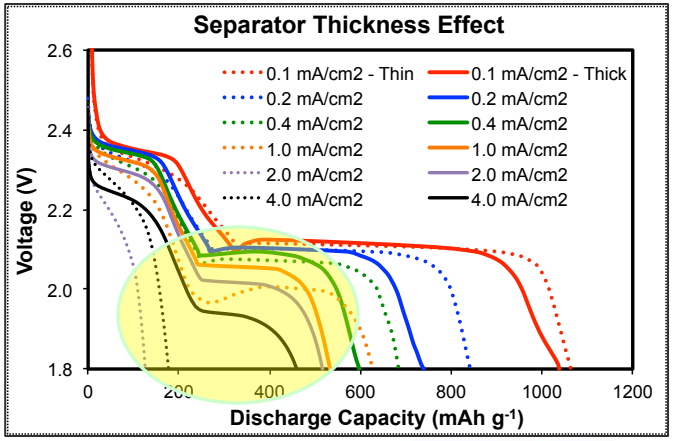


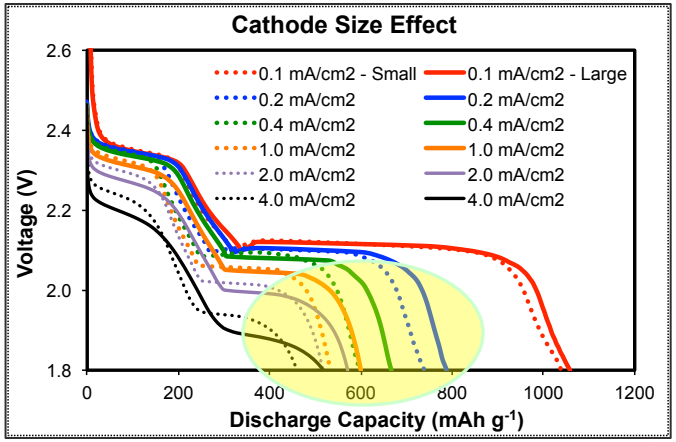
- Completed preliminary cell design factor screening test.
- Strong influence of cell design factors on cell electrochemical performance uncovered.
- Systematic cell design study initiated.

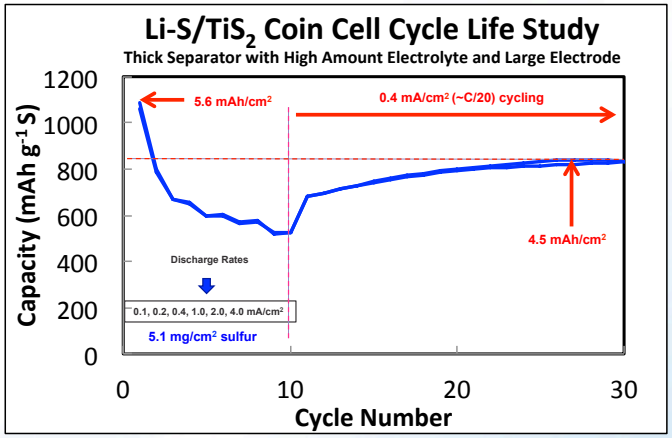
Accomplishments and Progress

Cell design optimization – electrolyte amount and location







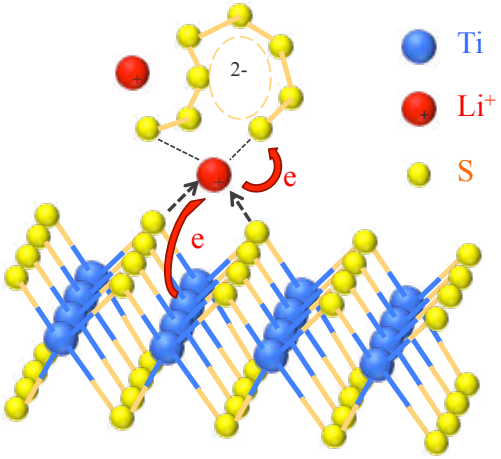


- Cell design factor screening study achieved ~**840 mAh g^{-1} sulfur** utilization (or ~ **470 mAh g^{-1} electrode**) and ~**4.5 mAh cm^{-2}** areal capacity under cycling at 0.4 mA cm^{-2} (~C/20) for **5.1 mg cm^{-2}** sulfur loading electrode.

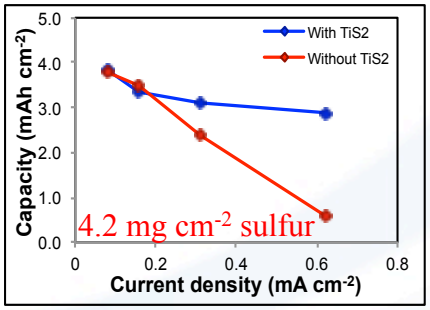
Accomplishments and Progress

Mechanism understanding (S-TiS_2 interaction)

- Polysulfide (PS) adsorption by TiS_2 has been hypothesized with theoretical prediction* and indirect experimental evidences.
- For the 1st time, the PS adsorption on the TiS_2 surface is directly detected in XPS experiment.**
- For TiS_2-PS surface interaction, electron density shifted from Ti to Li through sulfur in TiS_2 and shifted from Li to S in polysulfide based on the binding energy analysis of XPS.

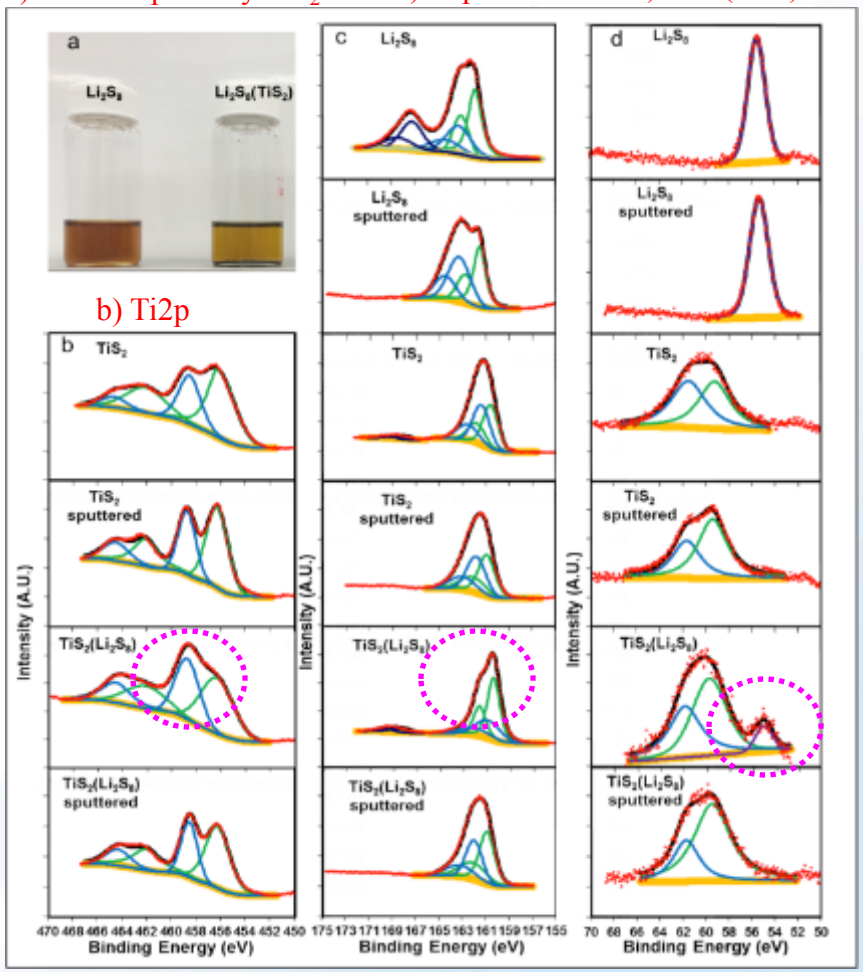


- The adsorption of PS on TiS_2 surface promotes the nucleation conversion of PS to Li_2S_2/Li_2S, leading to more efficient sulfur utilization at high discharge rate.



a) PS adsorption by TiS_2 c) S2p d) Li1s(Ti2s)

b) Ti2p



* Yi Cui's theoretical model: TiS_2-Li_2S_6 binding energy E_b = 1.02 eV (BMR FY2016 Q3 Report)

** Ke Sun, Qing Zhang, David C. Bock , Xiao Tong, Dong Su, Amy C. Marschilok, Kenneth J. Takeuchi, Esther S. Takeuchi and Hong Gan, *J. Electrochem. Soc.* Manuscript accepted for publication.

Responses to Previous Year Reviewers' Comments

- **Comment:** The reviewer commented that, in general, the approach is systematic and the topic important for addressing Li-S barriers. The reviewer observed that the baseline system may not be ideal because it comes with a number of problems unrelated to the area the project is addressing.
  - ***Response:*** Material screening studies was the focus in Phase I with unexpected behaviors and side reactions observed for several candidates (such as CuS and FeS_2). During Phase II, our research is more focused on the TiS_2, which shows beneficial interaction in Li-S cell system. System optimization studies have been conducted on the sulfur-TiS_2 system.
- **Comment:** The reviewer stated that the approach to improve S utilization through improved conductivity using additives is reasonable. The reviewer added that there are several issues that this approach will likely not address, like polysulfide dissolution and reaction at the Li-metal anode, and the need for large volumes of electrolytes that reduce Wh/kg values.
  - ***Response:*** Since this project is scoped to study sulfur cathode, our effort was not directed to anode protection and electrolyte. However, we have identified TiS_2 as the leading MFCA, which not only provides improved conductivity and electrochemical activity, it also acts to adsorb polysulfide as demonstrated during this year as part of the mechanism understanding effort – directly addressing the polysulfide dissolution issue. During this year, we start to look into the cell components interaction at the system level by expanding our studies on anode protection and new electrolyte investigation. Cell design issue relating to the electrolyte fill weight is also included in our study plan.
- **Comment:** The reviewer noted that a good amount of work was reported, but that most of the results are not of interest due to the low energies reported. For example, 300-500 mAh/g at 2 V is barely better than NMC, which cycles thousands of times.
  - ***Response:*** Boost the energy density at the cell level under high discharge rate is our goal. This year, we uncovered multiple cell design factors that strongly influence the cell delivered energy, such as sulfur loading, electrode density, electrolyte fill weight, the location of the electrolyte, uniform distribution of TiS_2, and discharge rate, etc. By optimizing the material and cell design parameters, we have demonstrated much higher sulfur utilization at 1100 mAh g^{-1} with sustainable cycling capacity at ~840 mAh g^{-1} sulfur, or ~ 4.5 mAh cm^{-2} areal delivered capacity, for a more realistic 5.1 mg cm^{-2} sulfur loading electrode (slide 13). We expect more improvement from our future work.

Responses to Previous Year Reviewers' Comments

- **Comment:** The reviewer stated that the project contributes to the understanding of benefits of transition metal sulfide additives, but could not identify a sulfide that adds significant value
  - ***Response:*** In our study we identified TiS_2 as the most effective MFCA last year. Based on this years research, it is determined that TiS_2 is electronically conductive, electrochemically active and has ability to adsorb polysulfide. In addition, it also acts as catalyst promoting the conversion of soluble polysulfide to the insoluble Li_2S_2/Li_2S, especially for the high sulfur loading electrode – resulting in significant cell discharge power improvement and lower capacity fade during cell cycling. All these characteristics make TiS_2 a truly Multi-Functional Cathode Additive. There are still more room for this system optimization and additional follow up research is planned for the future years.
- **Comment:** The reviewer noted that the team is concentrating on the most promising additive, TiS2, adding that it will be interesting to see if there are any new approaches to mitigating/reducing polysulfide dissolution
  - ***Response:*** During this year, we put more effort in understanding of how and why TiS_2 helps sulfur electrode electrochemical performance. Beside its high electronic conductivity and electrochemical activity, we proved experimentally by XPS that TiS_2 strongly interacts with polysulfide by absorbing the later on its surface. At the same time, it promotes the conversion of polysulfide to Li_2S_2/Li_2S. All the results point to the direction of maximizing the surface area of TiS_2. We plan to explore ways to prepare high surface area TiS_2 for additional system optimization. Furthermore, we have also initiated preliminary study on new electrolytes that also significantly reduce the polysulfide solubility with improved Li-S cell cycle life. We propose to systematically explore this area to aid system level interaction optimization effort.
- **Comment:** The reviewer pointed out that required system-level attention was recognized to efficiently investigate the beneficial sulfur/ TiS_2 interaction.
  - ***Response:*** We recognize the importance of system level interaction which must be addressed in order to achieve acceptable Li-S battery performance for commercialization. Although our project is primarily focused on the cathode optimization, we start to look into the other cell components and cell design parameters as part of our system level optimization effort. Very fruitful results have already been obtained from these preliminary studies. We plan to have focused study on other cell components in addition to our effort of S-TiS_2 hybrid cathode optimization. The combination of these efforts will result in the optimized Li-S cell performance at the system level.

Partners / Collaborations

- **Brookhaven National Laboratory (BNL)**
  - Dr. Hong Gan (PI) – Project coordination
  - Dr. Ke Sun – Project execution
- **Stony Brook University**
  - Prof. Esther Takeuchi (Co-PI), Prof. Amy Marschilok, Prof. Kenneth Takeuchi – Sample preparation for particle size studies, material characterization, *in operando* XRD study of S-TiS_2 hybrid cell discharge mechanism
- **Center of Functional Nanomaterials (CFN), BNL**
  - Dr. Dong Su – TEM/ED, SEM morphology and structural characterization
  - Dr. Xiao Tong – XPS analysis on S:TiS_2 interaction
  - Dr. Qin Wu – Modeling calculation for electrolyte solvent – solute interaction
- **National Synchrotron Light Source II, (NSLS II) BNL**
  - Prof. Yu-chen Karen Chen-Wiegart (Stony Brook University) – XRF and XPD studies on S-CuS interaction
  - Dr. Eric Dooryhee, Dr. Jianming Bai – XPD study on S-CuS interaction
  - Dr. Juergen Thieme – XRF study on S-CuS interaction
- **Columbia University**
  - Prof. Simon Billinge – PDF structural characterization on S:FeS interaction

Remaining Challenges and Barriers

- The mechanism and factors affecting the nucleation process of polysulfide to Li_2S_2/Li_2S are not well understood. Sulfur utilization at high rate discharge for high sulfur loading electrodes still need to be improved.
- Cell design factors, such as electrolyte fill volume and its location, have strong influence on the sulfur cell electrochemical performance. Strong interactions between cathode, anode and electrolyte at the system level and its impact on cell performance require more attention.
- It is a challenging task to maximize the beneficial interaction between polysulfide and TiS_2 additive, while at the same time maximizing sulfur content in the formulation for high energy density at the electrode level.
- Mechanical and electrochemical factors are not always working in the same direction, such as Ketjen Black is good for sulfur electrode electrochemical performance, but cannot achieve high sulfur loading electrode with the conventional slurry casting process.
- Polysulfide dissolution is still a major challenge for Li-S cell to achieve high energy efficiency and long cycle life. Electrolyte with low polysulfide solubility and low density (weight) is desirable for highly porous sulfur electrode to achieve high energy density at the cell level.
- Anode passivation by $LiNO_3$ limit the discharge voltage cut off to 1.8V, which prevent the nucleation process of polysulfide to Li_2S_2/Li_2S for high sulfur loading electrodes under high current density discharge. Alternative anode protection method need to be developed.
- Li anode low Coulombic efficiency, especially for high sulfur loading cells, negatively impact cell cycle life.

Proposed Future Research

FY17 On Going Milestones

- Complete cell design factor optimization with better understanding of cathode-anode-electrolyte interaction at the cell level. Complete cell activation study and prepare 4 mAh sample cells for confirmation study and for independent test samples delivery.

Proposed Future Research*

- Continue research on structurally stable additives, that do not involve conversion reaction during discharge and help the nucleation process of polysulfide to Li_2S_2/Li_2S, by focusing on the layered metal sulfide materials, such as TiS_2, MoS_2, WS_2, VS_2 and ZrS_2.
- Maximizing polysulfide adsorption on TiS_2 surface and the polysulfide to Li_2S_2/Li_2S nucleation kinetics for high sulfur utilization, especially with high sulfur loading (> 6 mg cm^{-2}) electrodes, by introducing high surface area (>10x) 2-dimensional (2D) transition metal sulfide additives, such as TiS_2 and MoS_2, etc.
- Optimizing sulfur – 2D TiS_2 hybrid cathode formulation with increased sulfur content and increased TiS_2 surface area to achieve improved electrode mechanical integrity and cell level energy density.
- Reducing polysulfide dissolution by developing new electrolyte systems and optimizing lean electrolyte cell designs with reduced electrolyte weight.
- Anode surface protection to minimize shuttling side reactions and to allow the high sulfur loading cells to be discharged to below 1.8V at high rate for high sulfur utilization.
- Developing alternative 3-D electrode processing capability to allow the use of Ketjen Black as carbon host with high sulfur loading, and with adjustable porosity for electrolyte location control to achieve optimum Li-S cell electrochemical performance.
- Mechanistic understanding of the sulfur cell components interaction by continuing developing *operando* cell characterization capabilities.

*Any proposed future work is subject to change based on funding levels.

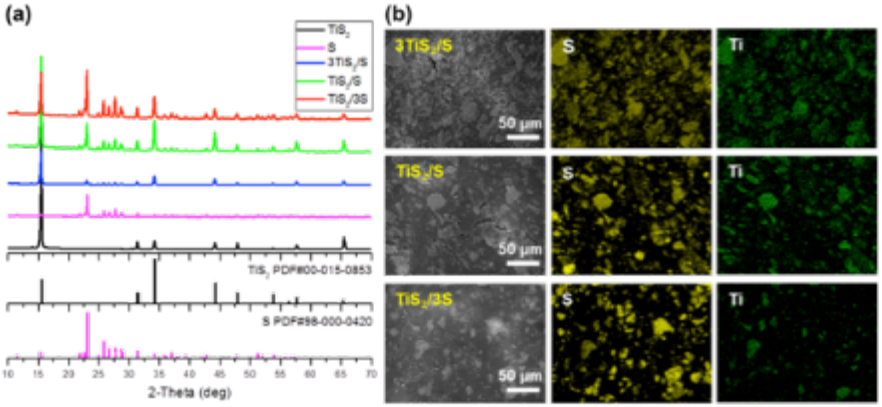
Summary

- TiS_2 is confirmed to be a beneficial multi-functional cathode additive for sulfur battery, contributing to the electrode reversible capacity during sulfur cell cycling with improved cell electrochemical performance – high rate and sulfur utilization, better cycle life.
- In-situ XRD study of S-TiS_2 hybrid electrodes confirmed the TiS_2 contribution in cell capacity and the improvement of cell discharge power.
- For the 1st time, direct experimental evidence of polysulfide-TiS_2 interaction is uncovered by XPS study, consistent with the theoretical prediction.
- Identified HPC as a new binder for sulfur electrode to achieve superior electrode to Al current collector adhesion and the electrode mechanical integrity.
- Commercially available low cost micro-porous carbon (A5597) with high pore volume has been identified as alternative carbon host to achieve high sulfur loading (up to 10 mg cm^{-2}) and good cell cycle life.
- Optimized S:TiS_2 hybrid formulation with energy density of 600 mAh g^{-1} at electrode level achieved in coin cell discharge.
- Demonstrated the impact of S:TiS_2 hybrid electrode loading, density and discharge current density on the coin cell electrochemical performance – optimized condition identified.
- Electrolyte fill weight and electrolyte location are uncovered to be important cell design factors that influence sulfur cell high rate electrochemical performance.
- Good coin cell cycling performance with 840 mAh g^{-1} sulfur, or 4.5 mAh cm^{-2} has been achieved for high sulfur loading electrode (5.1 mg cm^{-2}) at ~ C/20 rate.
- Tube cell designed for *operando* synchrotron characterization of sulfur-CuS hybrid system clearly identified the cell reaction mechanism and the interaction between the multiple cell components.
- With diffraction based technique, Li_2FeS_2 is directly detected for the first time as a reaction intermediate in electrochemical cells with FeS:S hybrid electrode using Pair Distribution Function analysis.

Technical Backup Slides

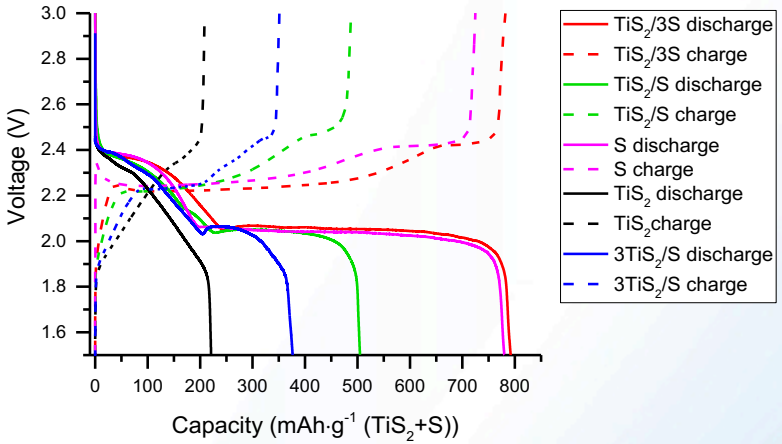
Accomplishments and Progress

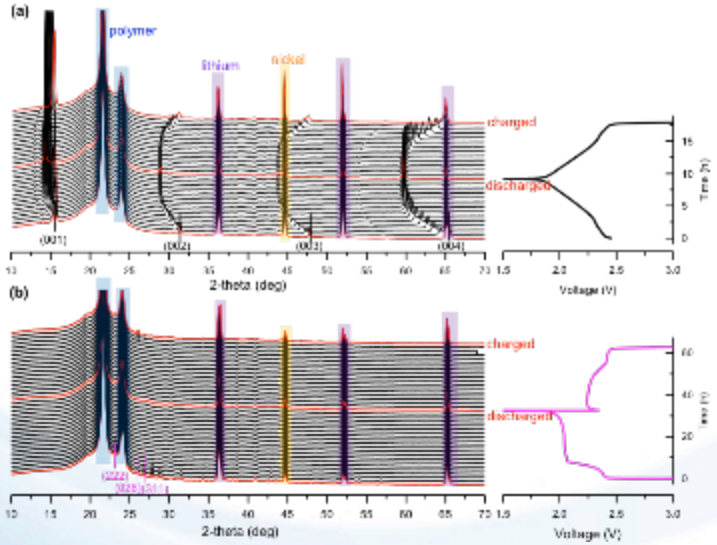
Mechanism understanding (S-TiS_2 in-situ XRD study)



(a) XRD and EDX map of (b) TiS_2-S composite electrodes

Discharge and charge profile of TiS_2-S electrodes





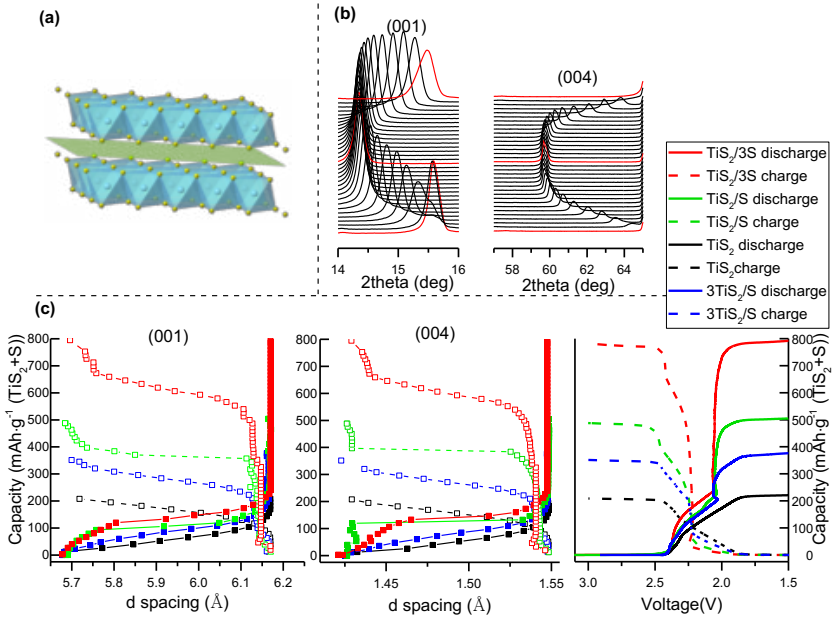
In-situ XRD data of (a) TiS_2 and (b) S electrode.

- Composite electrodes $3TiS_2$/S, TiS_2/S and TiS_2/3S contain only TiS_2 and S phases, and TiS_2 and S are dispersed well in the electrodes.
- $3TiS_2$/S showed the highest utilization of sulfur in the 2.4-2.0 V reaction voltage range, while TiS_2/3S showed the highest 2.1 V reaction efficiency and overall highest sulfur utilization.

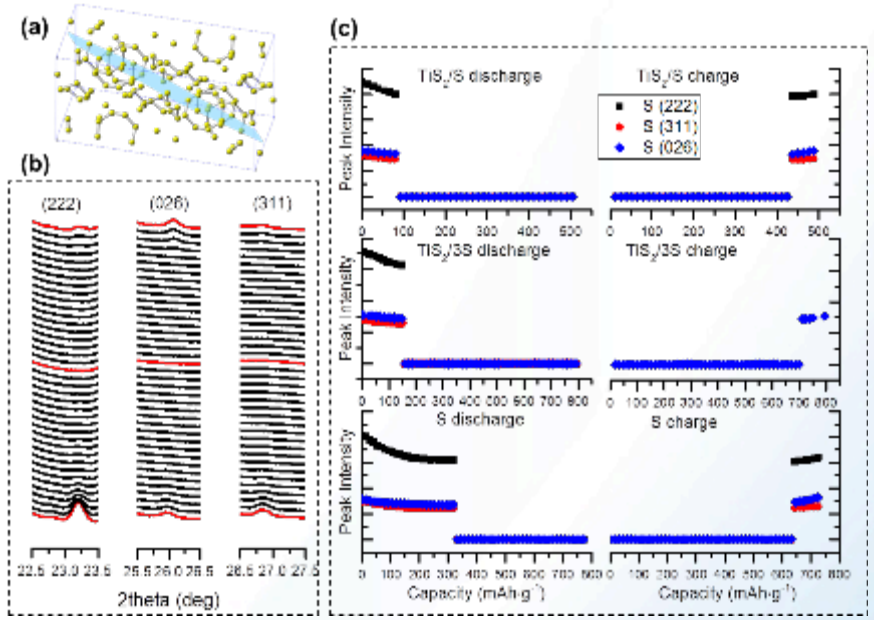
Q. Zhang, D. Bock, K. Takeuchi, A. Marschilok and E. Takeuchi, *J. Electrochem. Soc.*, 2017, 164, A897-A901.

Accomplishments and Progress

Mechanism understanding (S-TiS_2 in-situ XRD study)



(a) Crystal structure of TiS_2 (b) (001) and (004) peak evolution during TiS_2 discharge and charge (c) D-spacing change of TiS_2 (001) and (004) planes of TiS_2-containing samples.



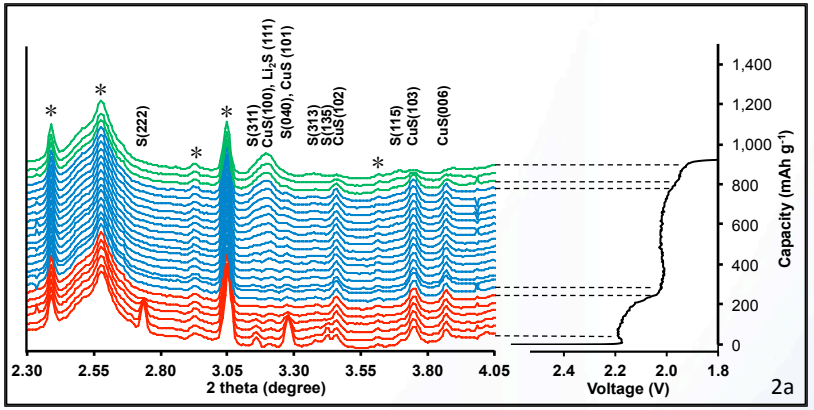
(a) Crystal structure of S_8 (b) Sulfur (222), (026) and (311) peak evolution during S discharge and charge (c) Sulfur peak intensity change with respect to discharge and charge capacity of TiS_2/S, TiS_2/3S, and S sample.

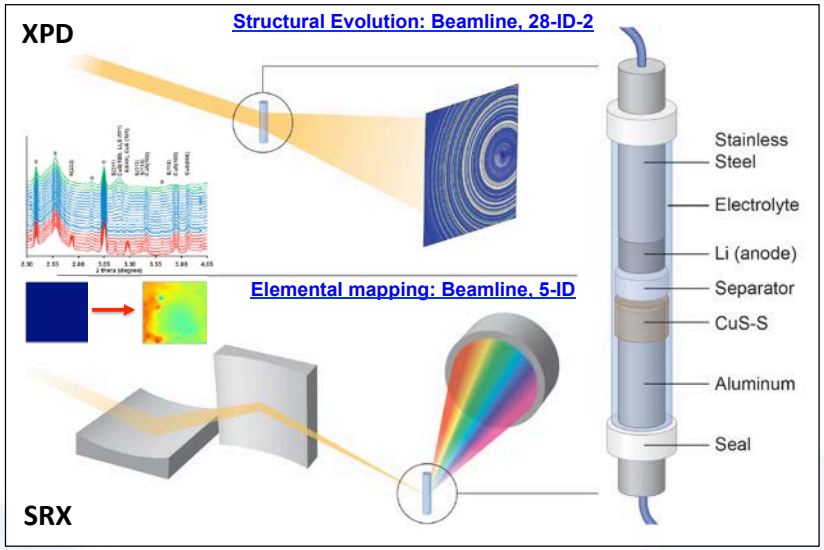
- TiS_2 and S discharge and charge simultaneously in TiS_2-S composite electrodes.
- Incorporation of TiS_2 can alleviate electrode polarization and improve the utilization of sulfur.

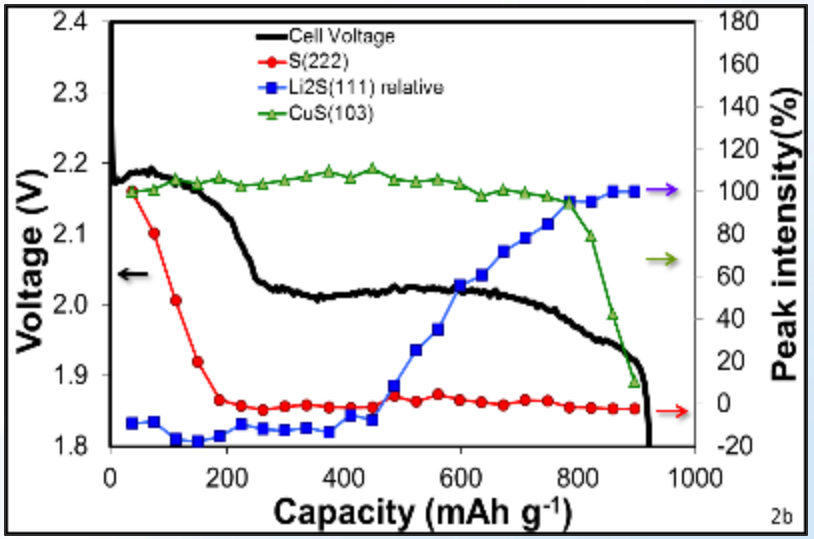
Accomplishments and Progress

Mechanism understanding (S-CuS interaction – *Operando* study)

- **Tube cell design:** Enabling synchrotron *operando* studies on cathode, anode, electrolyte and their interaction.
- **Multi-modal approach:** Combining spectroscopy (chemistry), diffraction (structure), and imaging (morphology and elemental distribution).





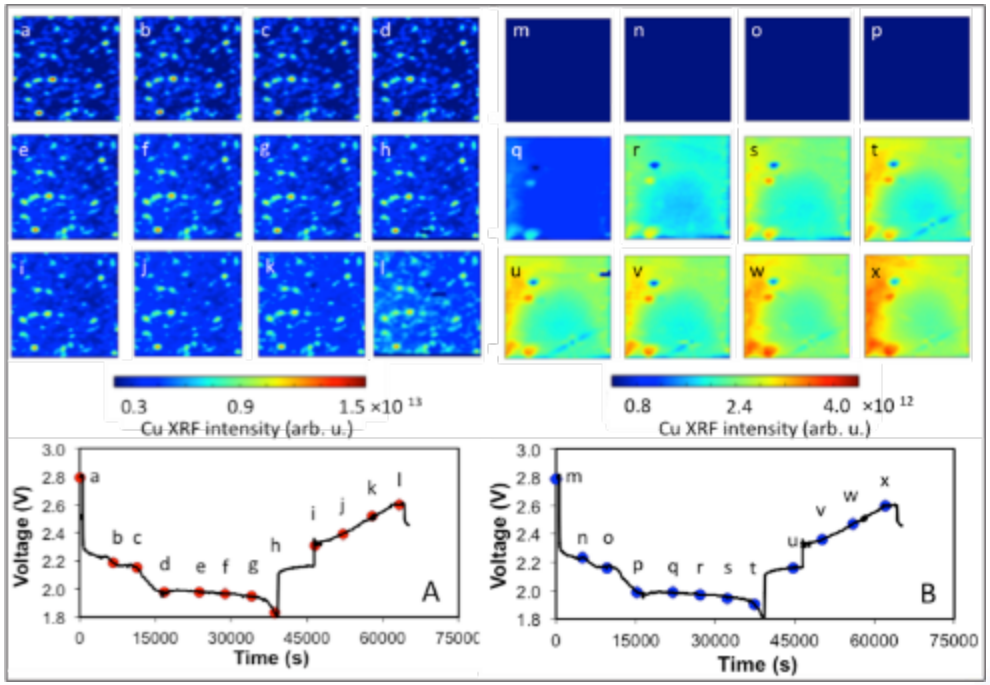


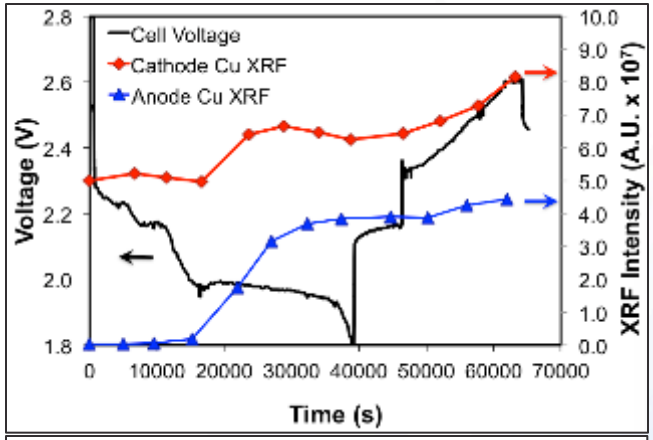
- *Operando* XPD study clearly identified the sequence of material phase transition of S-CuS hybrid cathode during cell discharge.

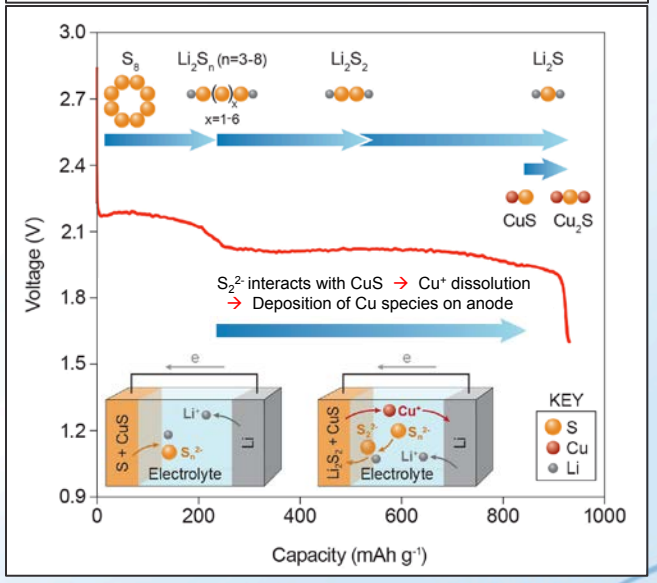
Accomplishments and Progress

Mechanism understanding (S-CuS interaction – *Operando* study)

Cu XRF mapping of cathode (A vs. a-l) and anode (B vs. m-x)



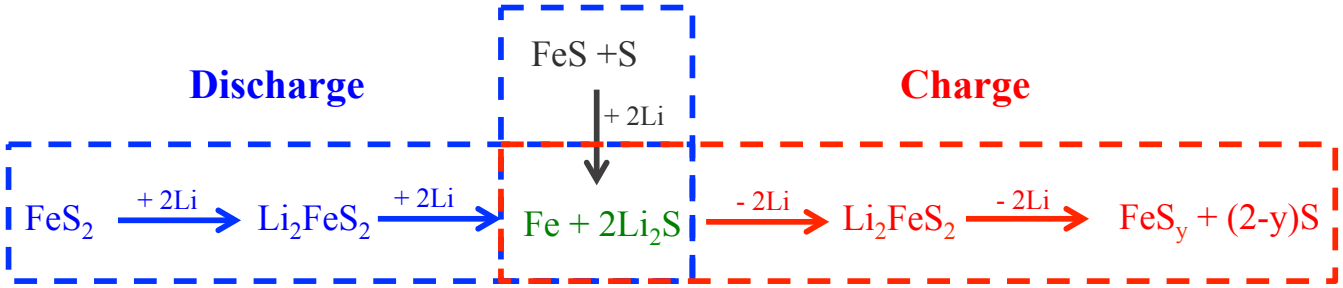


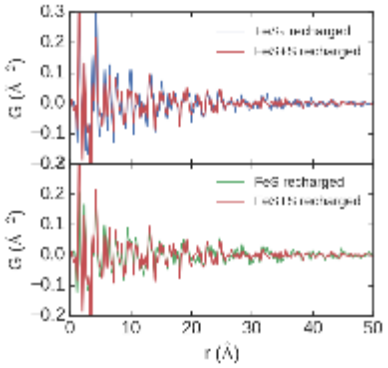


- *Operando* XRF imaging clearly shows how, when and where Cu migrates during S-CuS hybrid cathode tube cell discharge and charge.
- With XPD and XRF combined, the material phase changes and the dissolution mechanism of CuS in the S-CuS hybrid electrode are clearly elucidated.

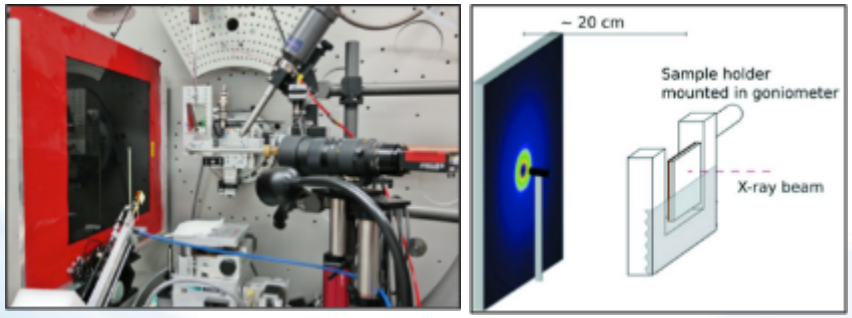
Accomplishments and Progress

Mechanism understanding (S-FeS interaction – PDF analysis)





- Strong interaction between sulfur and FeS in hybrid electrode is detected.
  - High flux, high energy *x-ray total scattering* at the XPD beamline allows for direct analysis of the electrode material in a transmission geometry. Pair distribution function (PDF) analysis enables direct, atomic resolution, quantification of disordered phase development in the electrodes.
  - Local structural changes are observed in FeS and FeS_2 electrode during cell cycling, and compared to a hybrid FeS:S system.



Experimental setup at beamline 28-ID-2 (XPD) at the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory.

- The electrode structures do not return to their original states after the first cycle.
- With diffraction based technique, Li_2FeS_2 is directly detected for the first time as a reaction intermediate in electrochemical cells.